NOVEL APPROACHES TO THE PRODUCTION OF HIGHER ALCOHOLS FROM SYNTHESIS GAS

Quarterly Technical Progress Report No. 8

For The Period July 1, 1992 to September 30, 1992

Contractor

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CONTRACT OBJECTIVES

Task 1.   Program Management.

Task 2.   Liquid-Phase, Higher Alcohol Process with Recycle of Lower Alcohols.

Task 3.   Novel Catalysts for Synthesis of Higher Alcohols.

Task 4.   Synthesis of Higher Alcohols via Acid-Base Catalysis.

Task 5.   Technology Evaluation.

SUMMARY

Task 2: A detailed technical plan for research on higher-alcohol synthesis in a slurry reactor was prepared and approved internally, as part of the University's requirements for the doctoral degree. The focus of this plan is the so-called "high-pressure" methanol synthesis catalyst, and modifications thereof. A major challenge of the research will be to identify a slurry medium that is stable at the typical operating temperature of this catalyst, i.e., about 400°C.

Two "shakedown" runs were made in the stirred autoclave without catalyst in order to check the mechanical operation of the system and to test some of the analytical equipment.

Task 3: Further preparation, characterization and screening of higher-oxygenate synthesis catalysts based on rhodium were carried out. The catalyst compositions tested during the period were: Rh/Al_2O_3, $Rh/Nb/Al_2O_3$, $Mo/Rh/Al_2O_3$ and $W/Rh/Al_2O_3$. All catalysts contained a nominal 1 wt. % Rh. $Rh/Nb/Al_2O_3$ and $Rh/Mo/Al_2O_3$ were about twice as active for CO conversion as the other catalysts. However, oxygenate yields were disappointing for all of the compositions tested. The $Rh/Mo/Al_2O_3$ catalyst had the highest carbon efficiency to oxygenates, 33%.

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TECHNICAL PROGRESS

A. Task 2:

    1) Research Proposal

As part of the requirements for the Ph.D. in Chemical Engineering, a research plan was written which contains a literature review, initial calculations and results, and a detailed research plan for the synthesis of higher alcohols from CO and H_2 in a slurry reactor. The full text of this plan is in Appendix A. The rationale and thrust of the proposed work is summarized below.

Methanol is presently produced from syngas over a Cu/ZnO "low pressure" methanol synthesis catalyst in fixed-bed reactors. Air Products has advanced methanol synthesis technology by demonstrating the use of a slurry reactor, as opposed to fixed-bed reactors. The slurry reactor offers three distinct advantages over the fixed-bed: 1) superior heat transfer and mixing characteristics, which maintain isothermal reactor conditions, decreasing thermal deactivation of catalysts; 2) the ability to operate with CO-rich synthesis gas, and; 3) tolerance of smaller catalyst particle sizes which eliminates the need for catalyst pelletizing and provides increased degrees of freedom in catalyst design. A pilot scale facility at LaPorte, TX operated by Air Products can produce up to 13 tons/day of methanol from synthesis gas.

Higher alcohol synthesis (HAS) from syngas has been investigated for many years, but existing HAS catalysts are characterized by poor selectivity to higher alcohols, typically >50%, and low activity. Although many catalysts have been investigated, none have been used commercially. However, a combination of some of the more promising HAS catalysts with the slurry reactor technology could yield a viable process for higher alcohol synthesis.

After an extensive review of the performance of current HAS catalysts, it was concluded that one of the more selective and active catalysts is an alkali-promoted ZnCr oxide, i.e., an alkali-promoted version of the so-called "high pressure" methanol synthesis catalyst that was used before development of the Cu/ZnO "low pressure" catalyst. Previous research has shown that pure ZnO catalyzes chain growth, while the chromium and the alkali promoter apparently steer the catalyst toward higher alcohol selectivity. However, pure Cr oxide does not have HAS activity. Replacement of the Cr with Mo,

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which is a proven HAS catalyst, could yield higher selectivity and activity for higher alcohol synthesis. Based on these results, and on Air Products' demonstration of slurry reactor technology, a research proposal was developed as follows:

- Construct slurry reactor system with appropriate analytical system;

- Verify operating procedures by using a BASF Cu/ZnO methanol synthesis catalyst with known results;

- Ensure reactor behaves as an ideal continuous stirred tank reactor, and that no mass transfer limitations exist in the reactor;

- Define a slurry medium that will be stable at 400°C in the presence of H_2 and catayst;

- Establish commercial ZnCrO methanol catalyst performance in slurry reactor;

- Examine effects of product recycle to encourage HAS;

- Synthesize and test ZnMo and MnCr oxide catalysts as possible HAS catalysts;

- Promote the most promising catalyst with Cs, determine optimum Cs concentration for HAS;

- If none of the catalysts tested appear promising, promote the ZnCrO methanol catalyst with Cs, determine optimum Cs concentration for HAS in a slurry reactor;

- Develop a kinetic model for the system studied.

2) Blank Runs

A "blank" run was conducted in July using a 2/1 H_2 to CO ratio with the hydrogen flowrate at 3300 sccm. The reactor was charged with Drakeol 10B slurry medium, but no catalyst was present. Compressor seal failure ended the run after only 12 hours. The compressor was sent to the manufacturer for repair.

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The blank run was designed to determine whether any reactions, especially methanation, are occurring in the system. Also, the run allowed the analytical system to be tested. The Poroplot Q column was unable to separate hydrogen, nitrogen, and carbon monoxide. However, a MolSieve 5A column does separate these gases, so a new column/valve configuration, as shown in Figure 1, was developed to optimize the gas sample separation and identification. Two sample loops operate in parallel, sending one sample to the MolSieve 5A column and thermal conductivity detector (TCD), and the other to a Poroplot Q column connected to the flame ionization detector (FID). The MolSieve 5A separates permanent gases such as N_2, H_2, CO, CO_2 and CH_4. The Poroplot Q separates hydrocarbons and alcohols. The MolSieve is subsequently backflushed through a Poroplot Q column after the last gas (CO_2) is detected. This allows water detection since water is held up by the MolSieve 5A.

A second "blank" run lasting about two days was performed in the slurry reactor system in August. The system was operated at "typical" methanol synthesis conditions, but again without catalyst in the reactor. The operating conditions were:

Reactor Temperature: 250°C
Reactor Pressure: 750 psig
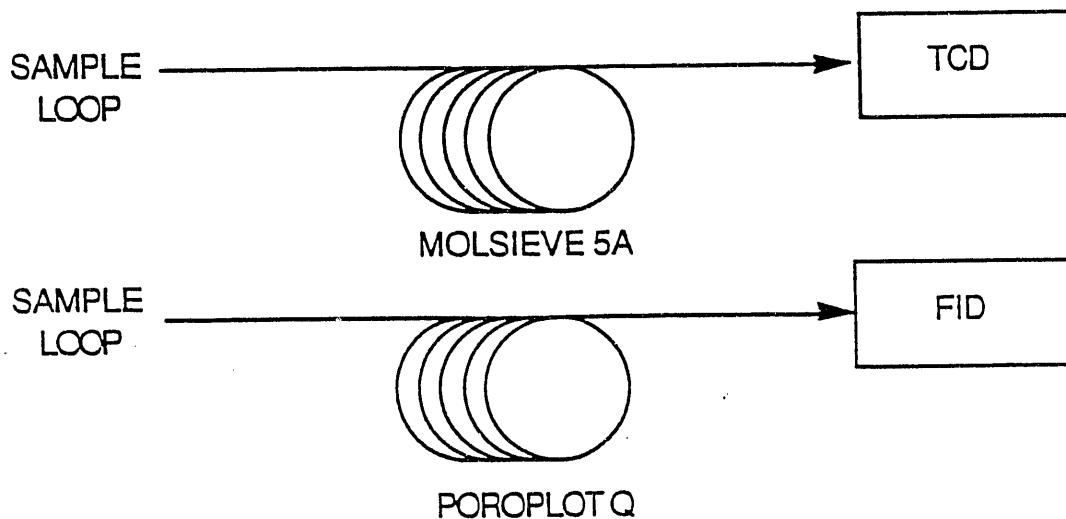Slurry Medium: Penreco Drakeol 10B
H_2/CO ratio: 1
Feed Rates: 550 standard cm^3/min for each component (H_2 and CO)

No methane was detected by gas chromatography during the 48 hour run, indicating that the methanation reaction did not take place as a result of a catalytic effect intrinsic to the equipment. Moreover, no other products, e.g., CO_2, C_2H_6 and higher hydrocarbons, were detected, suggesting that reactions such as hydrocracking of the oil and carbon formation did not occur. However, several problems were revealed during the run:
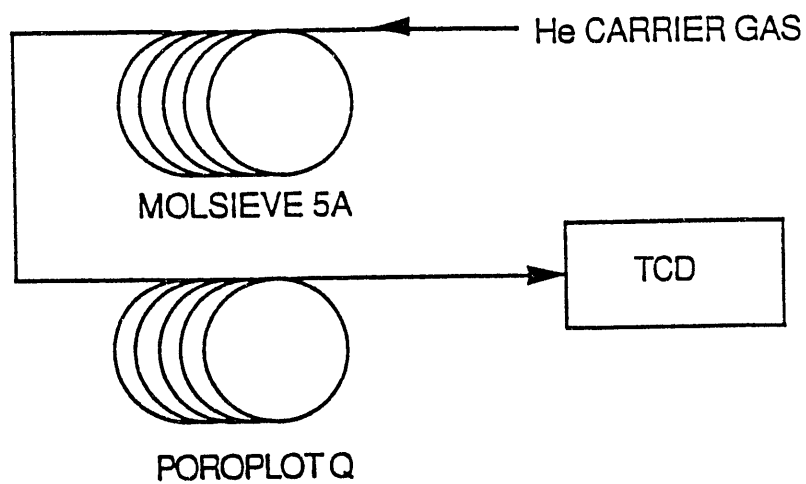
- Hydrogen Detection - With helium as a carrier gas, hydrogen detection was not sufficiently sensitive for quantitative purposes. Since the thermal conductivity difference between argon and hydrogen is much larger than that of helium and hydrogen, argon will be tested as a substitute carrier gas.

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FIGURE 1

GAS CHROMATOGRAPH CONFIGURATION

INJECT POSITION

SAMPLE
LOOP ────────────────→ TCD

MOLSIEVE 5A

SAMPLE
LOOP ────────────────→ FID

POROPLOT Q

COLUMN BACKFLUSH

←──── He CARRIER GAS

MOLSIEVE 5A

────────────────→ TCD

POROPLOT Q

- Mass Balance Inaccuracies - Two complete mass balances were performed during the blank run, and a minimum 50% error occurred in the mass in versus mass out determinations. Complete re-calibrations of the mass flow controllers and the wet test meter will be performed before the next run.

- Oil Retention - After the run, only 20 ml of Drakeol remained in the reactor; 175 ml of oil drained from the separator, and the remaining 100 ml is believed to have been carried out with the gas or lost during reactor depressurization. The separator located after the reactor will discharge its liquid contents directly back to the reactor, so the oil is not lost. Also, reactor depressurization must be done slowly to ensure no significant liquid discharge.

B) Task 3:

Syngas conversion to oxygenates was studied on rhodium on alumina (Rh/Al_2O_3) catalysts using niobium (Nb), molybdenum (Mo), and tungsten (W) as promoters. These catalysts were prepared either by impregnating Al_2O_3 with an aqueous solution of metallic salt, using the incipient wetness technique, or by adsorption of organometallic precursors onto Al_2O_3 or by combinations of these two techniques. The catalysts were characterized using Infrared (IR) spectroscopy and Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy.

The literature provides a rationale for studying Nb as a promoter in supported Rh/Al_2O_3 catalysts, with the goal of increased CO hydrogenation selectivity to higher oxygenates. Ichikawa has reported that supported Rh catalysts derived from $[Rh_4(CO)_{12}]$ on Nb_2O_5 produced C_2^+ oxygenates from $CO + H_2$ at atmospheric pressure with a carbon efficiency (CE) of 39%[1]. In our work, the desired $Rh/Nb/Al_2O_3$ catalyst structure was highly dispersed Rh clusters supported on a NbO_x monolayer covering a high-surface-area alumina (NbO_x/Al_2O_3).

In addition to Nb, Mo and W were also used as promoters in Rh/Al_2O_3

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[1] Ichikawa, M., Bull. Chem. Soc. Jpn., **51**, 2268-2273 (1978); Chem. Tech., 674 (1982).

catalysts. The desired catalyst structure in this case was bimetallic clusters of Rh with Mo or W on high-surface-area alumina support.

Table 1 shows the catalyst compositions that were synthesized and the results of testing these catalysts for higher-alcohol-synthesis (HAS) activity. For a given Rh deposition technique, either impregnation with $Rh(NO_3)_3$ or decomposition of $[Rh_4(CO)_{12}]$, $Rh/Nb/Al_2O_3$ was more active than Rh/Al_2O_3 by about a factor of 2. The selectivity of both of these catalyst compositions was not satisfactory, since the carbon efficiency for oxygenates was only 11 to 25% for all four catalysts tested. However, for a given composition, the oxygenate selectivity of the cluster-derived catalyst was somewhat higher than that of impregnated (salt-derived) catalyst, although this effect is more pronounced for Rh/Al_2O_3 than for $Rh/Nb/Al_2O_3$. Relative to the comparable Rh/Al_2O_3 catalyst, the $Rh/Nb/Al_2O_3$ catalyst produced a higher ratio of

C_2^+/C_1 oxygenates and a significantly lower ratio of alcohols to aldehydes.

The $Mo/Rh/Al_2O_3$ catalyst was slightly less active for CO conversion than the $Rh/Nb/Al_2O_3$ catalyst, but the carbon efficiency for oxygenates was significantly higher, 33% overall and 26% for C_2^+ oxygenates. The alcohol/aldehyde ratio for the $Mo/Rh/Al_2O_3$ catalyst was about 5 times that of the $Rh/Nb/Al_2O_3$ catalyst, suggesting that the former had much higher hydrogenation activity.

The activity and oxygenate selectivity of the $W/Rh/Al_2O_3$ catalyst were about the same as those for Rh/Al_2O_3.

EXAFS spectroscopy characterization of the Rh/Al_2O_3 and $Rh/Nb/Al_2O_3$ catalysts is summarized in Table 2. These results show that the cluster-derived Rh/Al_2O_3 and $Rh/Nb/Al_2O_3$ catalysts that were pretreated at 200°C for 1 hr. in helium had equivalent Rh-Rh coordination numbers, suggesting that the Rh dispersion, i.e., the Rh surface area, is similar for these two catalysts. If so, the observed two-fold difference in activity between these two catalysts reflects a higher turnover frequency for the $Rh/Nb/Al_2O_3$ catalyst. It may be that oxophilic Nb is able to promote CO dissociation, perhaps by bonding with oxygen of adsorbed CO to form a Rh-CO-Nb species. The data in Table 2 for the cluster-derived Rh/Al_2O_3 catalyst also suggest that Rh dispersion decreases, i.e., the coordination number increases, when the pretreatment conditions become more severe, i.e., 250°C in H_2/CO versus 200°C in He.

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The EXAFS data also indicate that Rh is more highly dispersed (lower coordination number) on the Nb-promoted catalyst derived from $Rh(NO_3)_3$ than it is on the same catalyst derived from Rh carbonyl, despite the fact that the impregnated catalyst was activated at more severe conditions. However, the higher dispersion of the impregnated $Rh/Nb/Al_2O_3$ catalyst did not result in a higher catalyst activity; both catalysts gave about the same CO conversion.

Rh reduction on the $Rh/Nb/Al_2O_3$ catalyst derived from $Rh(NO_3)_3$ appeared to be incomplete since each Rh on this catalyst appeared to be coordinated with about 0.70 oxygen atoms at a distance of about 2 angstroms. No Rh-O bonds were detected on the salt-derived Rh/Al_2O_3 catalyst.

In the cluster-derived catalysts, approximately one carbon (or oxygen) atom was found to be associated with each Rh at unusually short distances of 0.9 to 1.7 angstroms. Although it is difficult to discriminate between carbon and oxygen atoms, it seems probable that the atoms detected are carbon resulting from disproportionation of the carbon monoxide in the original carbonyl complex.

Figures 2, 3 and 4 show the Fourier Transform Infra Red (FTIR) spectra in the CO-stretching region of three Rh-containing catalysts and their precursors. Figure 2 shows the spectra for a Rh/Al_2O_3 catalyst derived from $Rh_4(CO)_{12}$. The "as synthesized" spectrum contains a peak at about 2100 cm^{-1} which corresponds to CO linearly adsorbed on Rh. The peak at 1840 cm^{-1} corresponds to bridged CO. When the "as synthesized" catalyst was heated to 100°C, the bridged CO peak disappeared and the only significant peaks were the Rh^I geminal dicarbonyl peaks at about 2090 and 2040 cm^{-1}. This form of CO adsorption is usually found only on finely dispersed Rh particles, a result that is consistent with the EXAFS data discussed earlier.

In Figure 3, the upper spectrum, of $Mo(CO)_6$ adsorbed on Rh/Al_2O_3, is complex. The peaks at 2090 and 2040 cm^{-1} show CO adsorbed on Rh as the gem dicarbonyl. The peak at 2060 cm^{-1} probably shows linear CO adsorption on Rh, but may also indicate some linear adsorption on Mo. This spectrum suggests that Rh catalyzes the decomposition of $Mo(CO)_6$. The $Mo(CO)_6/Rh/Al_2O_3$ sample was then heated to 400°C for 1 hr. in vacuum to

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remove the CO. After cooling to 60°C, it was exposed to 50 torr CO and evacuated. The resulting spectrum showed a pronounced peak for the Rh gem-dicarbonyl species and a minor quantity of linearly-adsorbed CO, probably on Rh.

When $W(CO)_6$ was adsorbed on Rh/Al_2O_3, the upper spectrum in Figure 4 showed mainly linear CO adsorbed on W(ca. 2060 cm^{-1}). When this catalyst was treated as described in the paragraph above, a pronounced Rh gem-dicarbonyl peak was observed, along with a less pronounced linearly-adsorbed CO peak, probably on Rh.

Table 1
Syngas Conversion to Oxygenates on Promoted Rh/Al$_2$O$_3$ Catalysts[3]

| | Conversion | Yield (based on carbon efficiency) | | | | Alcohol to Aldehyde |
| | | Hydrocarbons | | Oxygenates[6] | | |
(#) Composition	%CO	C$_1$	C$_2^+$	C$_1$	C$_2^+$	Ratio
IMPREGNATED CATALYSTS[1,2] [Rh(NO$_3$)$_3$, Nb(HC$_2$O$_4$)$_7$ precursors]						
(1) 1%Rh/Al$_2$O$_3$	2.0	62	27	6	5	0.88
(2) 1%Rh/3%Nb/Al$_2$O$_3$	3.9	60	27	1	12	0.12
CLUSTER-DERIVED CATALYSTS[1,2] [Rh$_4$(CO)$_{12}$, Nb(HC$_2$O$_4$)$_7$ precursors]						
(3) 1%Rh/Al$_2$O$_3$	2.2	62	13	8	17	0.40
(4) 1%Rh/3%Nb/Al$_2$O$_3$	4.2	61	21	2	16	0.14
MIXED-TECHNIQUE CATALYSTS[1,2] [Rh(NO$_3$)$_3$, Mo(CO)$_6$, W(CO)$_6$ precursors]						
(5) Mo/1%Rh/Al$_2$O$_3$[4]	3.6	53	14	8	25	0.63
(6) W/1%Rh/Al$_2$O$_3$[5]	2.2	64	17	2	17	0.48

Notes:

1 Details of catalyst preparation procedures are given in Appendix B.

2 Pretreatment conditions: Heated at 5°C/min to 200°C in 50 cc/min of He and held at this condition for 1 hr. In addition, Catalysts 1, 2, 5, and 6 were reduced at 400°C in H$_2$ for 1 hr. Pressurized and heated to reaction temperature under reaction gases.

3 Testing conditions: 30 atm, 250°C, 9000 1/kg/hr GHSV, H$_2$:CO=2, 0.5 gr. of catalyst.

4 Catalyst contained approximately 0.1 wt% Mo.

5 Catalyst contained approximately 1 wt% W.

6 In the July through September Monthly Reports, some C$_1$ oxygenates, mainly formaldehyde, were mistakenly counted as C$_2^+$ oxygenates. This error has been corrected in this table. Further minor changes in some numbers are due to averaging from repeat runs.

Table 2
Cluster Configuration and Geometry by EXAFS Spectroscopy
Promoted Rh/Al$_2$O$_3$ Catalysts

Catalyst	Rh-Rh		Rh-C/O		Conversion**
(Activation Conditions)	N*	R*	N*	R*	% CO
SALT-DERIVED CATALYSTS (Rh(NO$_3$)$_3$, Nb(HC$_2$O$_4$)$_7$ precursors)					
1%Rh/Al$_2$O$_3$					
(400°C, H$_2$, 1hr)	5.0	2.68			2.0
1%Rh/3%Nb/Al$_2$O$_3$					
(400°C, H$_2$, 1hr)	2.7	2.66	0.7	2.01	3.9
CLUSTER-DERIVED CATALYSTS (Rh$_4$(CO)$_{12}$, Nb(HC$_2$O$_4$)$_7$)					
1%Rh/Al$_2$O$_3$					
(200°C, He, 1hr)	4.3	2.67	1.2	1.94	2.2
(250°C, 1:1H$_2$:CO, 1hr)***	5.6	2.71	0.9	1.90	
1%Rh/3%Nb/Al$_2$O$_3$					
(200°C, He, 1.r)	4.2	2.67	1.7	1.95	4.2

*N: coordination no; R: bond distance (A°)

**From Table 1

***Subsequent to 200°C, He, 1hr.
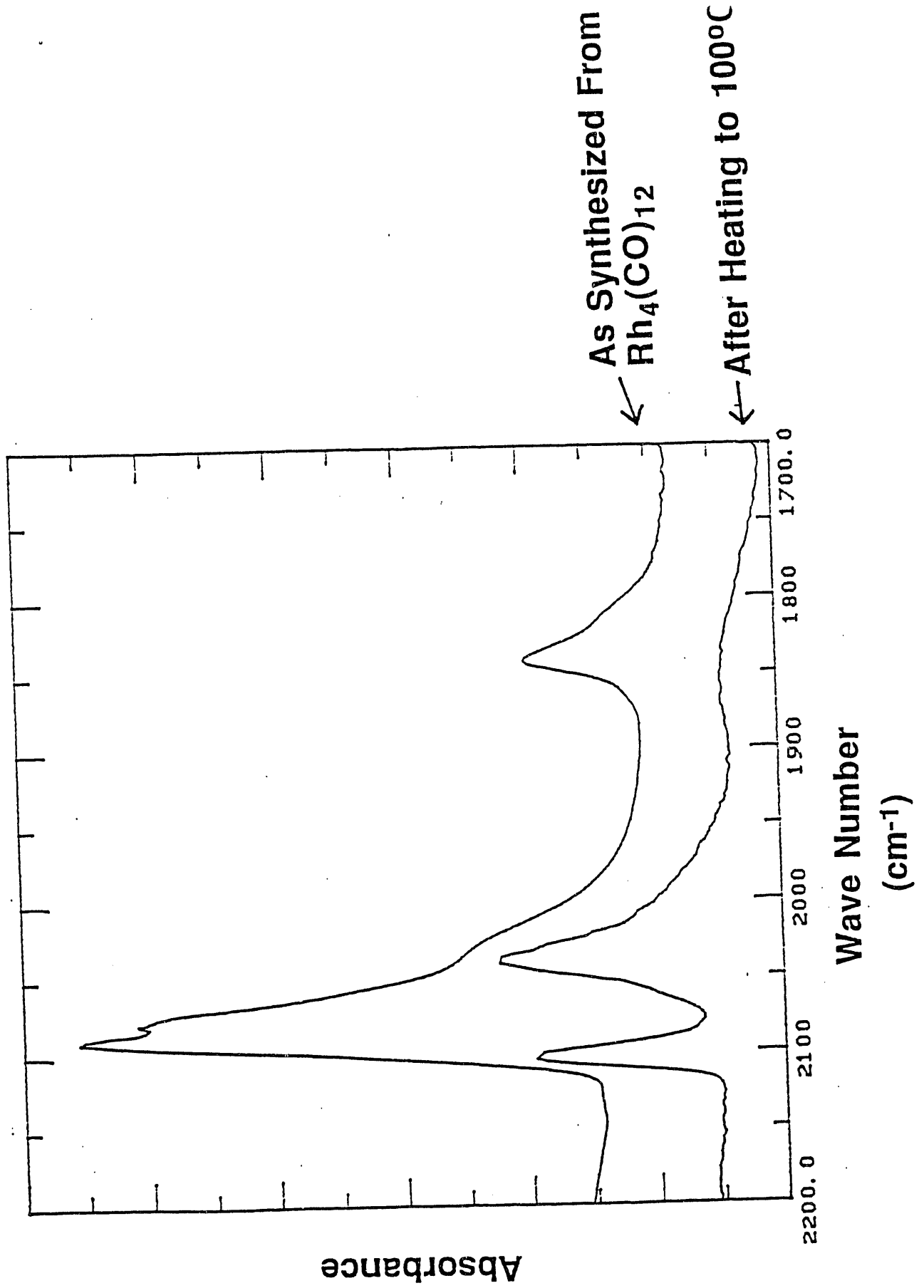
Figure 2

CO-IR Spectra for 1%Rh/Al₂O₃

As Synthesized From
Rh₄(CO)₁₂

After Heating to 100°C

Wave Number
(cm⁻¹)

Absorbance

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Figure 3

CO-IR Spectra for 0.06%Mo/1%Rh/Al₂O₃

After Mo(CO)₆ Adsorption at 60°C on Rh/Al₂O₃ and Evacuation

After Heating Mo/Rh/Al₂O₃ to 400°C in vacuum followed by CO Adsorption at 60°C and Evacuation

Wave Number (cm⁻¹)

Absorbance

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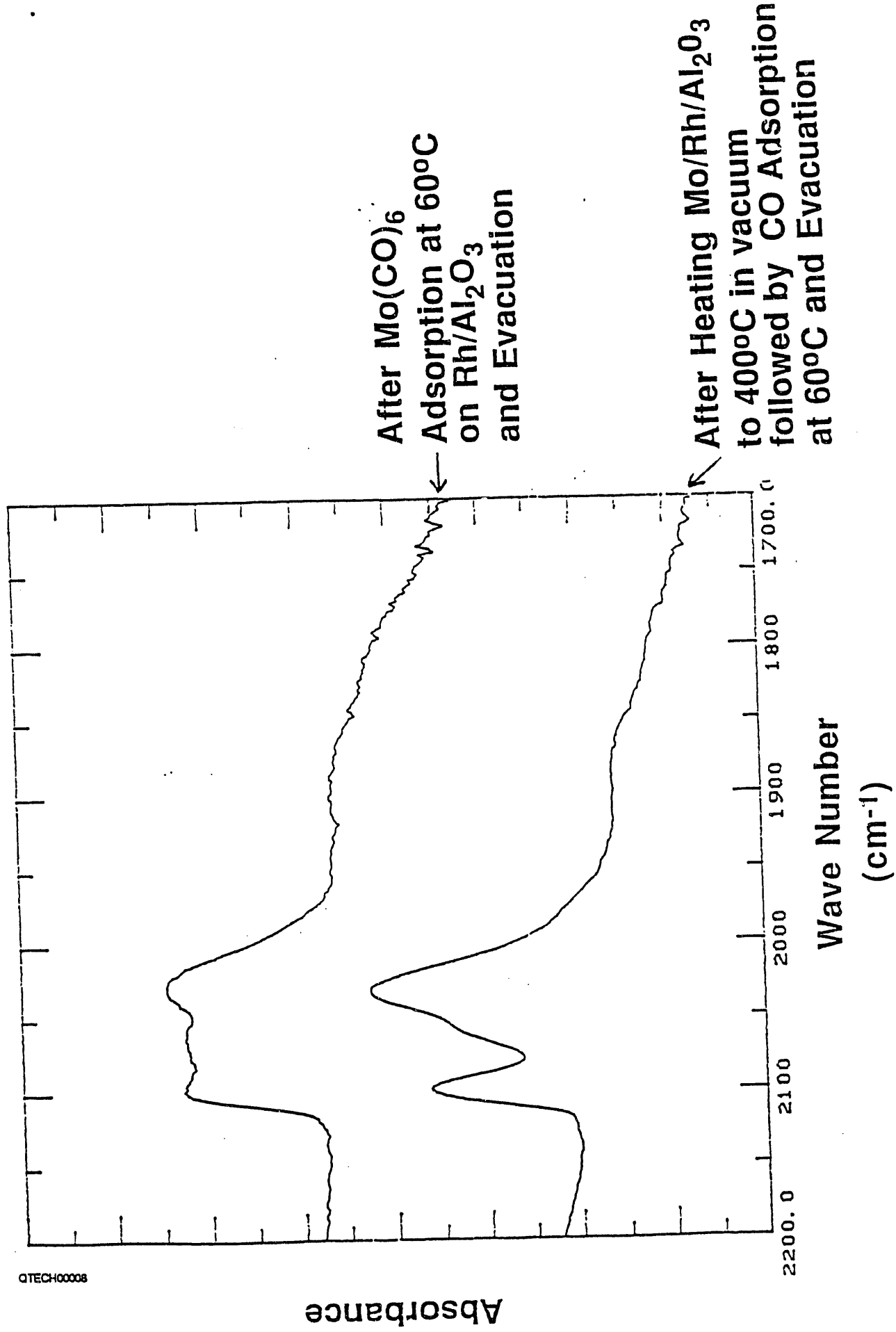
Figure 4

CO-IR Spectra for 1%W/1%Rh/Al₂O₃

After W(CO)₆ Adsorption and Evacuation

After Heating W/Rh/Al2O to 400°C followed by Adsorption and Evacuation

Wave Number (cm⁻¹)

Absorbance

QTECH00008
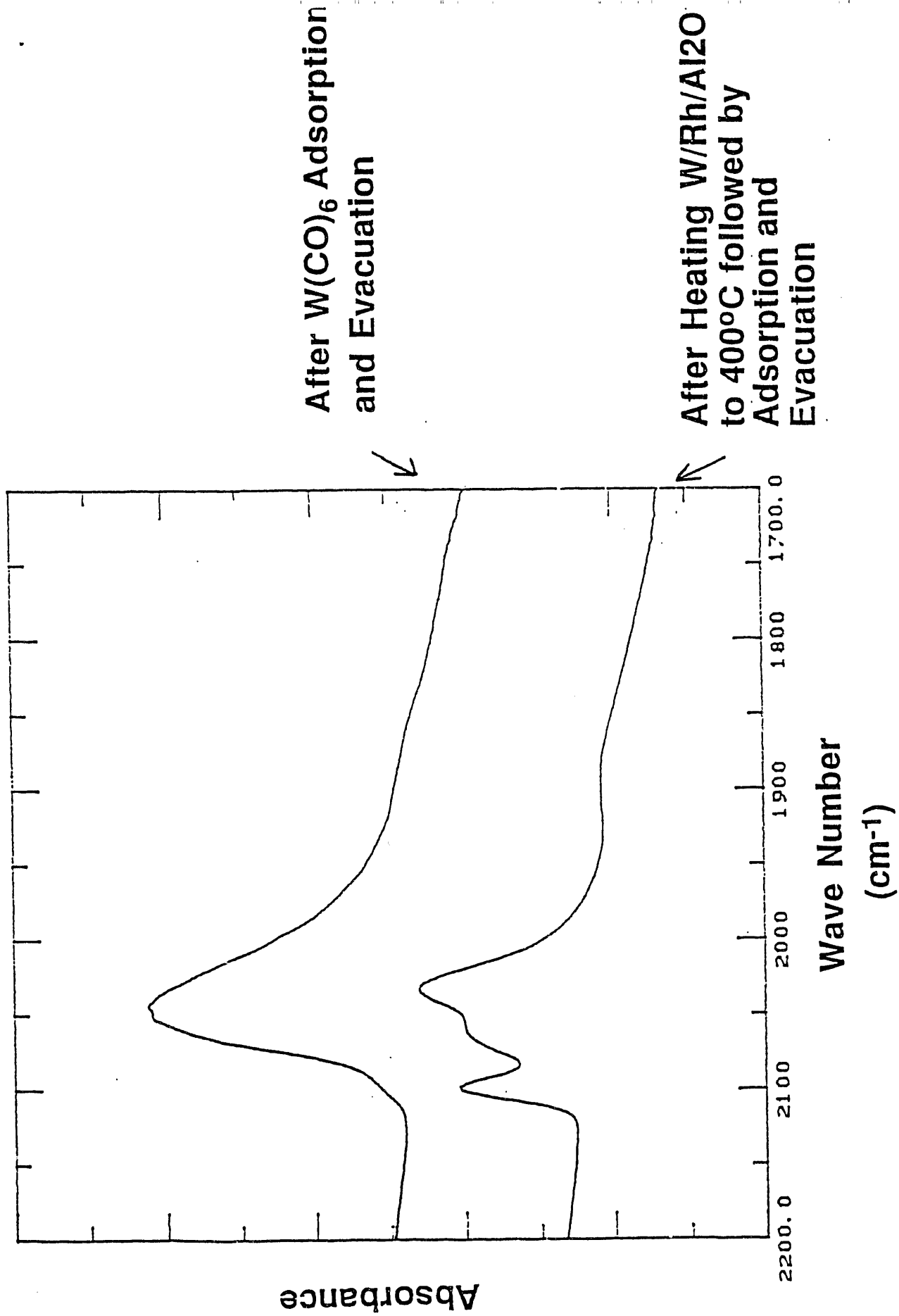
APPENDIX A

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